

FORM PTO-1390  
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

0020-4961P

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/069342

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/JP00/05673

August 24, 2000

August 25, 1999

TITLE OF INVENTION

LAMINATE COMPRISING FLUORINE-CONTAINING POLYMER

APPLICANT(S) FOR DO/EO/US

HIGUCHI, Tatsuya; OZAKI, Hidenori; KITAHARA, Takahiro; ISHIWARI, Kazuo

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau. WO 01/14141
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is transmitted herewith.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO-1449(s), and International Search Report (PCT/ISA/210) with 0 cited document(s).
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
  - 1.) PCT/IB/304 and PCT/IB/308
  - 2.) Zero (0) sheets of Formal Drawings

in, sec 37 CFR 1.5)

INTERNATIONAL APPLICATION NO

ATTORNEY'S DOCKET NUMBER

1069342

PCT/JP00/05673

0020-4961P

The following fees are submitted:

CALCULATIONS PTO USE ONLY

**NATIONAL FEE (37 CFR 1.492(a)(1)-(5):**

Other international preliminary examination fee (37 CFR 1.482)  
 or international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
 and International Search Report not prepared by the EPO or JPO. .... \$1,040.00

International preliminary examination fee (37 CFR 1.482) not paid to  
 USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
 but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. .... \$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
 but all claims did not satisfy provisions of PCT Article 33(1)-(4). .... \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
 and all claims satisfied provisions of PCT Article 33(1)-(4). .... \$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total Claims	15 - 20 =	0	X \$18.00
Independent Claims	1 - 3 =	0	X \$84.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable) None + \$280.00

**TOTAL OF ABOVE CALCULATIONS =**

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are  
 reduced by 1/2.

**SUBTOTAL =**

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
 months from the earliest claimed priority date (37 CFR 1.492(f)).

**TOTAL NATIONAL FEE =**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

**TOTAL FEES ENCLOSED =**

Amount to be:  
 refunded \$  
 charged \$

- i. ☒ A check in the amount of \$ **930.00** to cover the above fees is enclosed.
- j. ☐ Please charge my Deposit Account. No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
 A duplicate copy of this sheet is enclosed.
- k. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
 overpayment to Deposit Account No. 02-2448.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Send all correspondence to:

Birch, Stewart, Kolasch & Birch, LLP or Customer No. 2292  
 P.O. Box 747  
 Falls Church, VA 22040-0747  
 (703) 205-8000

Date: February 25, 2002

By Andrew D. Meikle  
 (Andrew D. Meikle, #32,868)

10/069342

JC19 Rec'd PCT/PTO 25 FEB 2002

PATENT  
0020-4961P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: HIGUCHI, Tatsuya et al.  
Int'l. Appl. No.: PCT/JP00/05673  
Appl. No.: New Group:  
Filed: February 25, 2002 Examiner:  
For: LAMINATE COMPRISING FLUORINE-  
CONTAINING POLYMER

PRELIMINARY AMENDMENT

**BOX PATENT APPLICATION**

Assistant Commissioner for Patents  
Washington, DC 20231

February 25, 2002

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP00/05673 which has an International filing date of August 24, 2000, which designated the United States of America.--

**IN THE CLAIMS:**

Please amend the claims as follows:

3. (Amended) The laminate according to claim 1, wherein said tetrafluoroethylene copolymer comprises 40 to 81 % by mole of tetrafluoroethylene and 60 to 19 % by mole of other monomer.

4. (Amended) The laminate according to claim 1, wherein said tetrafluoroethylene copolymer has a melt flow rate of 1.0 to 100 g/10 minutes.

5. (Amended) The laminate according to claim 1, wherein said tetrafluoroethylene copolymer has a melt flow rate of 1.0 to 50 g/10 minutes.

6. (Amended) The laminate according to claim 1, wherein said tetrafluoroethylene copolymer has a critical shear rate of 10 to  $10^3 \text{ sec}^{-1}$  at 230°C.

7. (Amended) The laminate according to claim 1, wherein said tetrafluoroethylene copolymer comprises tetrafluoroethylene, ethylene, a fluorovinyl compound of the formula (I):



wherein Rf is a fluoroalkyl group having 2 to 10 carbon atoms, and hexafluoropropylene, in which a molar ratio of

tetrafluoroethylene to ethylene is from 40:60 to 90:10, the content of said fluorovinyl compound is from 0 to 10 % by mole (based on the whole copolymer) and the content of hexane is from 0 to 30 % by mole (based on the whole copolymer).

8. (Amended) The laminate according to claim 1, wherein said ethylene-vinyl acetate copolymer has a vinyl acetate content X (% by mole) and a saponification degree Y (%) of a methyl ester satisfy the following relationship:

$$X \times Y/100 \geq 10.0.$$

9. (Amended) The laminate according to claim 1, wherein said ethylene-vinyl acetate copolymer has a melt flow rate (200°C, 5 kg-load) of 0.5 to 100 g/10 minutes.

10. (Amended) A tubular member comprising a laminate according to claim 1.

12. (Amended) A container comprising a laminate according to claim 1.

14. (Amended) A film comprising a laminate according to claim 1.

15. (Amended) A sheet comprising a laminate according to claim 1.

**REMARKS**

The specification has been amended to provide a cross-reference to the previously filed International Application.

The amendment to the claims is merely to delete the multiple dependencies and to place the application into better form for examination. Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

Attached hereto is a marked-up version of the changes made to the application by this Amendment.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By   
Andrew D. Meikle, #32,868

ADM/cqc  
0020-4961P

P.O. Box 747  
Falls Church, VA 22040-0747  
(703) 205-8000

Attachment: VERSION WITH MARKINGS TO SHOW CHANGES MADE

(Rev. 02/21/02)

VERSION WITH MARKINGS TO SHOW CHANGES MADE

The claims have been amended as follows:

3. (Amended) The laminate according to claim 1 or 2, wherein said tetrafluoroethylene copolymer comprises 40 to 81 % by mole of tetrafluoroethylene and 60 to 19 % by mole of other monomer.

4. (Amended) The laminate according to [any one of claims 1 to 3]claim 1, wherein said tetrafluoroethylene copolymer has a melt flow rate of 1.0 to 100 g/10 minutes.

5. (Amended) The laminate according to [any one of claims 1 to 3]claim 1, wherein said tetrafluoroethylene copolymer has a melt flow rate of 1.0 to 50 g/10 minutes.

6. (Amended) The laminate according to [any one of claims 1 to 5]claim 1, wherein said tetrafluoroethylene copolymer has a critical shear rate of 10 to  $10^3 \text{ sec}^{-1}$  at 230°C.

7. (Amended) The laminate according to [any one of claims 1 to 6]claim 1, wherein said tetrafluoroethylene copolymer comprises tetrafluoroethylene, ethylene, a fluorovinyl compound of the formula (I):



wherein Rf is a fluoroalkyl group having 2 to 10 carbon atoms,

and hexafluoropropylene, in which a molar ratio of tetrafluoroethylene to ethylene is from 40:60 to 90:10, the content of said fluorovinyl compound is from 0 to 10 % by mole (based on the whole copolymer) and the content of hexane is from 0 to 30 % by mole (based on the whole copolymer).

8. (Amended) The laminate according to [any one of claims 1 to 7]claim 1, wherein said ethylene-vinyl acetate copolymer has a vinyl acetate content X (% by mole) and a saponification degree Y (%) of a methyl ester satisfy the following relationship:

$$X \times Y/100 \geq 10.0.$$

9. (Amended) The laminate according to [any one of claims 1 to 8]claim 1, wherein said ethylene-vinyl acetate copolymer has a melt flow rate (200°C, 5 kg-load) of 0.5 to 100 g/10 minutes.

10. (Amended) A tubular member comprising a laminate according to [any one of claims 1 to 9]claim 1.

12. (Amended) A container comprising a laminate according to [any one of claims 1 to 9]claim 1.

14. (Amended) A film comprising a laminate according to [any one of claims 1 to 9]claim 1.



15. (Amended) A sheet comprising a laminate according to  
[any one of claims 1 to 9]claim 1.

(Rev. 11/13/01)

## DESCRIPTION

LAMINATE COMPRISING FLUORINE-CONTAINING POLYMER

## 5 FIELD OF THE INVENTION

The present invention relates to a laminate comprising a fluorine-containing polymer. In particular, the present invention relates to a laminate comprising a layer of a tetrafluoroethylene copolymer having a carbonate group and a layer  
10 of a polyolefine resin.

## BACKGROUND ART

Fluorine-containing polymers are used in various applications since they have excellent heat resistance, chemical resistance, surface properties (e.g. low abrasion properties,  
15 etc.) and electrical insulating properties. However, the fluorine-containing polymers have generally insufficient mechanical strength or dimensional stability, or they are expensive.

Thus, various attempts such as the adhesion or lamination  
20 of the fluorine-containing polymer to other organic material or an inorganic material have been made to make the best use of advantages of the fluorine-containing polymers while minimizing their disadvantages.

However, the fluorine-containing polymers inherently have  
25 a low adhesion force so that it is difficult to adhere them directly to other material. Even if fusion bonding is tried, the adhesion strength is insufficient, or when a certain level of adhesion strength is attained, the adhesion force tends to vary with a kind

of a substrate. Thus, the reliability of the adhesion is often insufficient.

To adhere the fluorine-containing polymers to other material, the following methods are mainly discussed:

- 5           1. Physically roughening the surface of a substrate with sand bluster treatment, etc.;
2. Surface treatment of a fluorine-containing polymer by sodium etching, plasma treatment, photochemical treatment, etc.;
3. Adhesion with an adhesive.

10       The methods 1 and 2 require the treatment process and the treatment steps are complicated, and thus their productivity is low. In addition, in the methods 1 and 2, the kinds and shapes of the substrates are limited. Anyhow, the adhesion force achieved by the methods 1 and 2 is low, and the appearance of the resulting  
15       laminate tends to have some problems (e.g. coloring, flaws, etc.).

          Various adhesives to be used in the method 3 are examined. Conventional hydrocarbon base adhesives have insufficient adhesion properties, and their own heat resistance is insufficient. Therefore, such adhesives cannot generally withstand adhering  
20       conditions for the fluorine-containing polymers which require molding or processing at high temperature, and they suffer from delamination or coloration due to decomposition. The laminates using such adhesives cannot maintain the adhesion force due to the change of temperature and environment and lack reliability  
25       since their adhesive layers have insufficient heat resistance, chemical resistance or water resistance.

          Alternatively, adhesion with an adhesive or an adhesive composition comprising a fluorine-containing polymer having a

functional group is studied.

Prior arts disclose, as an adhesive, the use a fluorine-containing polymer to which a hydrocarbon monomer having a carboxyl group, a carboxylic anhydride group, an epoxy group or a hydrolyzable silyl group (e.g. maleic anhydride, vinyltrimethoxysilane, etc.) is grafted (e.g. JP-A-7-18035, JP-A-7-25952, JP-A-7-25954, JP-A-7-173230, JP-A-7-173446, JP-A-7-173447, etc.), or the use of a cured material of an adhesive composition containing a fluorine-containing copolymer which comprises a hydrocarbon monomer having a functional group such as hydroxyalkyl vinyl ether copolymerized with tetrafluoroethylene, chlorotrifluoroethylene, etc., and a isocyanate curing agent as an adhesive for adhering polyvinyl chloride to ETFE (ethylene-tetrafluoroethylene copolymer) which has been treated with corona discharge (e.g. JP-A-7-228848).

The adhesive or adhesive composition comprising the fluorine-containing polymer to which the functional hydrocarbon monomer is grafted or copolymerized has insufficient heat resistance. Thus, it is decomposed and foamed so that the adhesion strength decreases, or the layers are delaminated or colored, when it is processed together with the fluororesin or used at high temperature. The adhesive composition disclosed in JP-A-7-228848 requires the corona discharge treatment of the fluororesin.

Furthermore, it is reported to use a fluorine-containing polymer having a functional group, which is prepared by copolymerizing a perfluorovinyl ether having a carboxylic acid group or its derivative with a fluorine-containing monomer, as an adhesive or an adhesive composition. US Patent No. 4,916,020

discloses a laminate using a fluorine-containing polymer having a functional group which is introduced in the polymer by copolymerizing a perfluorovinyl ether having a carboxylic acid group or its derivative with tetrafluoroethylene, etc.

5        In this laminate, the above-described fluorine-containing polymer having a carboxylic acid group, etc. is laminated on other substrate such as a metal substrate through an adhesive resin such as an epoxy resin, a urethane resin, etc. Thus, the epoxy resin or the urethane resin has problems in its heat resistance, chemical  
10 resistance or solvent resistance when the laminate is used.

WO98/58973 (published on December 30, 1998) discloses a laminate comprising a layer of a tetrafluoroethylene copolymer having a terminal carbonate group, a layer of other material such as a thermoplastic resin, and an intermediate layer between them.

15        One example described in this WO publication is a laminate comprising an intermediate layer of an epoxy group-containing polyethylene when polyethylene is used as the other material.

When the layer of the tetrafluoroethylene copolymer having a terminal carbonate group and the polyethylene layer are adhered  
20 with the epoxy group-containing polyethylene, the initial adhesion force is high, but the adhesion force tends to decrease with time. In addition, the epoxy group-containing polyethylene itself has low resistance to fuel and is dissolved in the fuel. Thus, this laminate cannot be used to fabricate a tube or a tank  
25 for storing the fuel.

#### DISCLOSURE OF THE INVENTION

One object of the present invention is to provide a laminate which comprises a layer of a tetrafluoroethylene copolymer having

a carbonate group and a layer of a polyolefine resin strongly adhered each other, the adhesion strength of which does not decrease with time, and which has high resistance to fuel.

According to the present invention, the above object is  
5 achieved by a laminate comprising

(1) a layer of a tetrafluoroethylene copolymer comprising 30 to 81 % by mole of tetrafluoroethylene and 70 to 19 % by mole of at least one other monomer and having a carbonate group in a polymer chain or at a polymer chain terminal, which has a melt  
10 flow rate of 0.1 to 100 g/10 minutes (230°C, 5 kg-load) and a melting point of 90 to 230°C,

(2) a layer of an ethylene-vinyl acetate copolymer formed on one surface of the layer (1), which satisfies the following relationship:

$$15 \quad X \times Y/100 \geq 7.0$$

wherein X is a vinyl acetate content (% by mole) and Y is a saponification degree of a methyl ester (%), and

(3) a layer of a polyolefin resin formed on the layer (2).

The carbonate group contained in the tetrafluoroethylene  
20 copolymer to be used in the present invention is a group having a bond of the formula:  $-\text{OC}(=\text{O})\text{O}-$ , and a specific example of the carbonate group is a group of the formula:  $-\text{OC}(=\text{O})\text{O}-\text{R}$  wherein R is a hydrogen atom, an organic group (e.g. a  $\text{C}_1$ - $\text{C}_{20}$  alkyl group, a  $\text{C}_2$ - $\text{C}_{20}$  alkyl group having an ether linkage, etc.), or an element  
25 of the I, II or VII Group. Preferable examples of the carbonate group include  $-\text{OC}(=\text{O})\text{O}-\text{CH}_3$ ,  $-\text{OC}(=\text{O})\text{O}-\text{C}_3\text{H}_7$ ,  $-\text{OC}(=\text{O})\text{O}-\text{C}_8\text{H}_{17}$ ,  $-\text{OC}(=\text{O})\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ , and the like.

The tetrafluoroethylene copolymer having a carbonate group

at a polymer chain terminal means a tetrafluoroethylene polymer having a functional group comprising a carbonate group on at least one terminal of the polymer chain. The tetrafluoroethylene copolymer having a carbonate group in a polymer chain means a  
5 copolymer prepared by copolymerizing an ethylenically unsaturated monomer having a carbonate group and tetrafluoroethylene. One polymer chain may have the carbonate groups in the polymer chain and also at the polymer chain terminal.

Among these copolymers, the tetrafluoroethylene copolymer  
10 having a carbonate group at a polymer chain terminal is preferable since it does not remarkably deteriorate heat resistance, mechanical properties and chemical resistance, or it is advantageous from the viewpoint of productivity and cost.

A polymer having no carbonate group may be compounded in  
15 the tetrafluoroethylene copolymer having a carbonate group.

According to the present invention, it is necessary for the tetrafluoroethylene copolymer to be fusion bonded to the polyolefin layer as an opposite material for lamination at a temperature at which polyolefin is not thermally decomposed, and  
20 has a viscosity so that the copolymer can sufficiently flow at such a temperature. A preferred range of the fusion bonding temperature of polyolefin is from about 200 to 280°C. Thus, the tetrafluoroethylene copolymer used in the present invention should be melt and have a melt viscosity so that it can flow in  
25 this temperature range.

When it is desired to lower the permeability of a fuel, the tetrafluoroethylene copolymer having a high melting point, that is, a melt flow rate of 0.1 to 100 g/10 minutes (230°C, 5 kg-

load) and a melting point of 90 to 230°C is preferably used. When the other material has low heat resistance, the tetrafluoroethylene copolymer having a low melting point, that is, a melt flow rate of 0.1 to 100 g/10 minutes (200°C, 5 kg-load) and a melting point of 90 to 200°C is preferably used.

In the present invention, the melt flow rate (MFR) of the tetrafluoroethylene copolymer is preferably from 1.0 to 100 g/10 minutes, more preferably from 1.0 to 50 g/10 minutes.

Herein, the melt flow rate is measured at 200°C or 230°C under a load of 5 kg with an orifice diameter of 2 mm and a land length of 8 mm.

In addition, the tetrafluoroethylene copolymer used in the present invention has a critical shear rate of 10 to  $10^3 \text{ sec}^{-1}$  at 230°C, and can be molded at a lower temperature than conventional fluororesins. Because of such a critical shear rate, the tetrafluoroethylene copolymer used in the present invention can solely be molded to form a molded article in the form of a film or a tube and also coextrusion molded with the polyolefin resin.

In one preferred embodiment, the tetrafluoroethylene copolymer used in the present invention has a monomer composition comprising 40 to 81 % by mole of tetrafluoroethylene (TFE) and 60 to 19 % by mole of other monomer, in particular, 40 to 81 % by mole of TFE, 6 to 43 % by mole of ethylene (Et) and 0 to 30 % by mole of hexafluoropropylene (HFP).

More preferably, the monomer composition comprises 40 to 60 % by mole of TFE, 24 to 43 % by mole of Et and 5 to 30 % by mole of HFP, since a polymerization decreases as the content of TFE increases.



The melting point of the tetrafluoroethylene copolymer used in the present invention continuously decreases and its crystallinity decreases so that its transparency increases, as the content of HFP increases.

5 In another preferred embodiment, in addition to TFE, Et and HFP, the tetrafluoroethylene copolymer used in the present invention may contain, as a modifier monomer, a fluorovinyl compound of the formula (I):

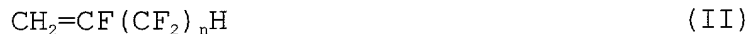


10 wherein Rf is a fluoroalkyl group having 2 to 10 carbon atoms.

When the number of carbon atoms of Rf is less than 2, the modification of the tetrafluoroethylene copolymer (for example, the suppression of cracking of molded articles during molding of the copolymer or in use) may be insufficient. When the number of carbon atoms of Rf exceeds 10, the compound (I) may be  
15 disadvantageous from the viewpoint of polymerization reactivity. In particular, Rf having 3 to 5 carbon atom is preferable.

From the viewpoint of the heat resistance of the copolymer obtained, the Rf group is most preferably a perfluoroalkyl group,  
20 or a  $\omega$ -hydro- or  $\omega$ -chloroperfluoroalkyl group.

Among those fluorovinyl compounds, a fluorovinyl compound of the formula (II):

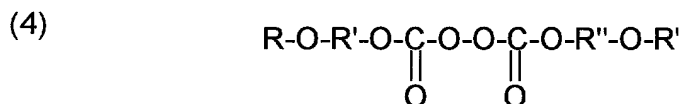
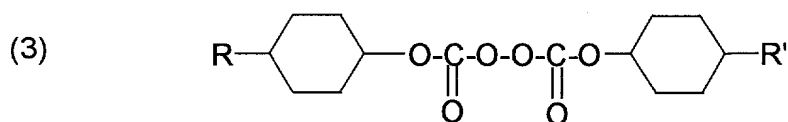
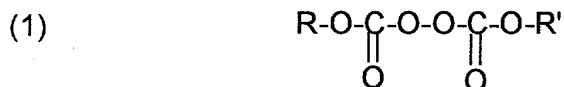


wherein n is a number of 2 to 10, in particular, a number of 3  
25 to 5 is preferable from the viewpoint of copolymerizability, costs for the preparation of the copolymer, and the properties of the copolymer obtained.

When the fluorovinyl compound (I) is used as a modifier monomer, a monomer composition is such that a molar ratio of tetrafluoroethylene to ethylene is from 40:60 to 90:10, the content of the fluorovinyl compound is from 0 to 10 % by mole (based on the whole copolymer) and the content of hexane is from 0 to 30 % by mole (based on the whole copolymer).

The tetrafluoroethylene copolymer of the present invention can be prepared by a polymerization process which is used to prepare ETFE.

To introduce the carbonate group at the chain terminal, a peroxy carbonate is used as a polymerization initiator in the preparation of the tetrafluoroethylene copolymer of the present invention. Examples of the peroxy carbonate include the following compounds (1) to (4):



wherein R and R' represent independently each other a monovalent

saturated straight or branched hydrocarbon group having 1 to 15 carbon atoms or a monovalent saturated straight or branched hydrocarbon having 1 to 15 carbon atoms and an alkoxyl group at the end of the molecule, and R" is a divalent saturated straight or branched hydrocarbon group having 1 to 15 carbon atoms or a divalent saturated straight or branched hydrocarbon having 1 to 15 carbon atoms and an alkoxyl group at the end of the molecule.

In particular, diisopropyl peroxydicarbonate, di-n-propyl peroxydicarbonate, tert.-butylperoxyisopropyl carbonate, bis(4-tert.-butylcyclohexyl) peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, etc. are preferable.

Industrially, the polymerization is preferably carried out by suspension polymerization in an aqueous medium using a fluorine-containing solvent and a peroxycarbonate as a polymerization initiator, although other polymerization methods such as solution polymerization, bulk polymerization, etc. may be employed.

Examples of the fluorine-containing solvent include hydrochlorofluoroalkanes (e.g.  $\text{CH}_3\text{CClF}_2$ ,  $\text{CH}_3\text{CCl}_2\text{F}$ ,  $\text{CF}_3\text{CF}_2\text{CCl}_2\text{H}$ ,  $\text{CF}_2\text{ClCF}_2\text{CFHCl}$ , etc.), chlorofluoroalkanes (e.g.  $\text{CF}_2\text{ClCFClCF}_2\text{CF}_3$ ,  $\text{CF}_3\text{CFClCFClCF}_3$ , etc.), and perfluoroalkanes (e.g. perfluorocyclobutane,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$ ,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ ,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ , etc.). Among them, the perfluoroalkanes are preferable.

The amount of the solvent used is preferably from 10 to 100 % by weight based on water from the viewpoint of suspending properties and costs.

The polymerization temperature is not limited, and is

preferably from 0 to 100°C.

The polymerization pressure may be determined according to other polymerization conditions such as the kind, amount and vapor pressure of the solvent used, the polymerization temperature, etc.

5 Usually, the polymerization pressure may be from 0 to 50 kgf/cm<sup>2</sup>G.

In the preparation of the tetrafluoroethylene copolymer of the present invention, a conventional chain transfer agent, for example, a hydrocarbon such as isopentane, n-pentane, n-hexane, cyclohexane; an alcohol such as methanol, ethanol, etc.; and a  
10 halohydrocarbon such as carbon tetrachloride, chloroform, methylene chloride, methyl chloride, etc., can be used to adjust the molecular weight.

As the ethylene-vinyl acetate copolymers, those having various contents of vinyl acetate and various saponification  
15 degrees are commercially available. Thus, from those ethylene-vinyl acetate copolymers, one satisfying the relationship of  $X \times Y/100 \geq 7.0$

wherein X is a vinyl acetate content (% by mole) and Y is a saponification degree of a methyl ester(%)  
20 can be selected.

For example, EVAL 101, which is available from KURARAY Co., Ltd., has a vinyl acetate content of 68 % and a saponification degree of 95 %. Thus,  $X \times Y/100$  is 4.6. MELSEN H6051, which is available from TOSO CORPORATION, has a vinyl content of 11.2 %  
25 and a saponification degree of 100 %. Thus,  $X \times Y/100$  is 11.2. TECHNOLINK K200, which is available from TAOKA Chemical Co., Ltd., has a vinyl acetate content of 11.2 % and a saponification degree of 85 %. Thus,  $X \times Y/100$  is 9.52. They are all ethylene-vinyl

acetate copolymers which can be used according to the present invention.

The melt flow rate (200°C, 5 kg-load) is from 0.5 to 100 g/10 minutes, preferably from 1.0 to 50g/10 minutes.

5        The viscosity of the ethylene-vinyl acetate copolymer is preferably close to that of the tetrafluoroethylene copolymer. When the difference of the viscosities of the two copolymers is large, the thickness of either the layer of the tetrafluoroethylene copolymer or the layer of the ethylene-vinyl  
10 acetate copolymer may become uneven. Therefore, the melt flow rate of the ethylene-vinyl acetate copolymer is preferably in the above range.

As the polyolefin resin, preferably polyethylene, polystyrene, polypropylene, polybutene, ethylene-vinyl acetate  
15 copolymer (EVA), ethylene-methyl acetate copolymer, ethylene-ethyl acrylate copolymer, ethylene-ethyl acrylate-maleic anhydride copolymer, and the like are used. In particular, polyethylene is preferable.

To increase the adhesion strength between the ethylene-vinyl acetate copolymer layer (2) and the polyolefin resin layer  
20 (3), a known adhesive olefin (e.g. maleic anhydride-modified polyethylene, maleic anhydride-modified polypropylene, etc.), maleic anhydride-modified polystyrene, and the like may be used as an adhesive.

25        Each of the layers of the laminate according to the present invention may contain an additive which is suitable for each polymer such as a reinforcing agent, a filler, a stabilizer, a UV ray absorber, a pigment, etc. insofar as the characteristics

of each layer are not deteriorated.

Such an additive can improve heat stability, surface hardness, abrasion resistance, antistatic properties, weather resistance, or other properties.

5        A method for producing the laminate of the present invention may be properly selected in accordance with the kind of the tetrafluoroethylene copolymer, the kinds of the materials used to form other layers, etc.

10        For example, the polymeric materials which form the respective layers are multilayer coextruded to form all the layers at one time to produce a molded article in the form of a film, a sheet, a tube, a hose, a bottle, a tank, etc.

#### EXAMPLES

##### Example 1

15        Pellets of a fluorine-containing polymer (monomer composition (molar ratio: TFE/Et/HFP/H2P ( $\text{CH}_2=\text{CF}(\text{CF}_2)_3\text{H}$ ) = 46.2/35.8/17.5/0.5; melting point: 158°C; MFR: 20 g/10 min. (230°C, 5 kg-load)) were charged in a mold having a diameter of 120 mm, and the mold is set in a press heated at 230°C, and the polymer  
20        was melt pressed under a pressure of about 50 kgf/cm<sup>2</sup> to obtain a sheet having a thickness of 0.5 mm.

Separately, each of an ethylene-vinyl alcohol copolymer (EVOH) (EVAL F 101A available from KURARAY Co., Ltd.; vinyl acetate content X: 68 % by mole; saponification degree: 95 %;  $X \times Y/100$   
25        = 64.6), maleic anhydride-modified polyethylene (ADOMER NF 528 available from MITSUI CHEMICALS, INC.) and high density polyethylene (BATEC-HD HJ560 available from Japan Polychem Corporation) was pressed at 230°C in the same manner as above to

obtain a sheet having a thickness of 0.5 mm.

Then, the four sheets obtained in the above steps were laminated in the order of the fluorine-containing polymer/ethylene-vinyl alcohol copolymer/maleic anhydride-modified polyethylene/high density polyethylene with inserting a polyimide film as a spacer partly between the fluorine-containing polymer sheet and the ethylene-vinyl alcohol copolymer sheet, and the laminate was placed in a mold having a diameter of 120 mm. The mold was set in a press heated at 230°C and the laminate was pressed for 10 seconds under a pressure of 10 kgf/cm<sup>2</sup> to fusion bond the sheets.

The polyimide film spacer was removed, and the unbonded parts were provided as grasping parts in an adhesion strength test. Then, a maximum peel strength (initial) and a fuel-resistant strength were measured by a T-shape peeling test method with a Tensilon general tester (manufactured by ORIENTEC Co., Ltd.).

As a fuel-resistant strength, a maximum peel strength was used, which was measured after dipping the sample in a fuel (CM15: a mixture of isoocatane and toluene in a volume ratio of 50:50 containing 15 % by volume of methanol) at 60°C for 168 hours.

The results are shown in Table 1.

Examples 2-3 and Comparative Examples 1-4

A sheet was produced in the same manner as in Example 1 except that the layer structure was changed and the materials of each layer were selected as described below. The results are shown in Table 1.

(Example 2)

Layer structure: TFE copolymer layer/ethylene-vinyl

acetate copolymer layer/polyolefin layer

TFE copolymer: the same as Example 1

Ethylene-vinyl acetate copolymer: EVOH (MELSEN H6051, available from TOSO CORPORATION; acetate content X: 11.2 %;

5 saponification degree: 100 %;  $X \times Y/100$ : 11.2)

Polyolefin: low density polyethylene (PETROCENE 292 available from TOSO CORPORATION)

(Comparative Example 1)

10 Layer structure: TFE copolymer layer/epoxy group-containing polyethylene layer/polyolefin layer

TFE copolymer: the same as Example 1

Epoxy group-containing polyethylene: epoxy-modified polyethylene (LEX PERL RA3150 available from Nippon Polyolefins Co., Ltd.)

15 Polyolefin: polyethylene (UBE POLYETHYLENE L519 available from Ube Industries, Ltd.)

(Example 3)

Layer structure: the same as Example 1

20 The same as those used in Example 1 except that EVOH (TECHNOLINK K200 available from TAOKA Chemical Co., Ltd.; vinyl acetate content: 11.2 %; saponification degree: 85 %;  $X \times Y/100$ : 9.52) being used as an ethylene-vinyl acetate copolymer layer.

(Comparative Example 2)

Layer structure: the same as Example 1

25 The same as those used in Example 1 except that EVOH (MELSEN H 6410M available from TOSO CORPORATION; vinyl acetate content: 11.2 %; saponification degree: 40 %;  $X \times Y/100$ : 4.48) being used as an ethylene-vinyl acetate copolymer layer.



(Comparative Example 3)

Layer structure: the same as Example 1

The same as those used in Example 1 except that EVA  
(ULTRACENE 540 available from TOSO CORPORATION; vinyl acetate  
5 content: 3.5 %; saponification degree: 0 %; X x Y/100: 0) being  
used as an ethylene-vinyl acetate copolymer layer.

(Comparative Example 4)

Layer structure: the same as Example 1

As a TFE copolymer, one prepared as follows was used:

10 The powder of the fluorine-containing polymer used in  
Example 1 (190 kg) and pure water (200 liters) were charged in  
a stainless steel tank. To the mixture, 28 % aqueous ammonia was  
added and then the mixture was stirred at 80°C for 5 hours while  
stirring. The powdery material was recovered from the tank,  
15 washed with water and dried to obtain a powdery polymer.

Table 1

	TFE copolymer	Adhesive layer (Et-vinyl acetate copolymer layer)	Maximum adhesive strength (initial) (kg/cm)	Adhesive strength after dipping in fuel (kg/cm)	Dissolving test of adhesive layer in fuel
Ex. 1	(Ex. 1)	EVOH X x Y/100 =64.6	Resin breakage >7.38	2.30	No dissolving
Ex. 2	(Ex. 1)	EVOH X x Y/100 =11.2	2.82	1.78	No dissolving
Comp. Ex. 1	(Ex. 1)	(Epoxy- modified polyethy- lene)	Resin breakage >4.06	X Spontaneously peeled due to dissolving of adhesive layer	Dissolved
Ex. 3	(Ex. 1)	EVOH X x Y/100 =9.52	2.64	X Spontaneously peeled due to dissolving of adhesive layer	Dissolved
Comp. Ex. 2	(Ex. 1)	EVOH X x Y/100 =4.48	X Sponta- neously peeled		Dissolved
Comp. Ex. 3	(Ex. 1)	EVA X x Y/100 =0	X Sponta- neously peeled		Dissolved
Comp. Ex. 4	(Ex. 1) (amide terminal)	EVOH X x Y/100 =64.6	X Sponta- neously peeled		No dissolving

## CLAIMS

1. A laminate comprising

(1) a layer of a tetrafluoroethylene copolymer comprising 30 to 81 % by mole of tetrafluoroethylene and 70 to 19 % by mole of at least one other monomer and having a carbonate group in a polymer chain or at a polymer chain terminal, which has a melt flow rate of 0.1 to 100 g/10 minutes (230°C, 5 kg-load) and a melting point of 90 to 230°C,

(2) a layer of an ethylene-vinyl acetate copolymer formed on one surface of the layer (1), which satisfies the following relationship:

$$X \times Y/100 \geq 7.0$$

wherein X is a vinyl acetate content (% by mole) and Y is a saponification degree of a methyl ester (%), and

(3) a layer of a polyolefin resin formed on the layer (2).

2. The laminate according to claim 1, wherein said tetrafluoroethylene copolymer of the layer (1) has a melt flow rate of 0.1 to 100 g/10 minutes (200°C, 5 kg-load) and a melting point of 90 to 200°C is preferably used.

3. The laminate according to claim 1 or 2, wherein said tetrafluoroethylene copolymer comprises 40 to 81 % by mole of tetrafluoroethylene and 60 to 19 % by mole of other monomer.

4. The laminate according to any one of claims 1 to 3, wherein said tetrafluoroethylene copolymer has a melt flow rate of 1.0 to 100 g/10 minutes.

5. The laminate according to any one of claims 1 to 3, wherein said tetrafluoroethylene copolymer has a melt flow rate of 1.0 to 50 g/10 minutes.

6. The laminate according to any one of claims 1 to 5, wherein said tetrafluoroethylene copolymer has a critical shear rate of 10 to  $10^3 \text{ sec}^{-1}$  at  $230^\circ\text{C}$ .

7. The laminate according to any one of claims 1 to 6, wherein  
5 said tetrafluoroethylene copolymer comprises tetrafluoroethylene, ethylene, a fluorovinyl compound of the formula (I):



wherein Rf is a fluoroalkyl group having 2 to 10 carbon atoms,  
10 and hexafluoropropylene, in which a molar ratio of tetrafluoroethylene to ethylene is from 40:60 to 90:10, the content of said fluorovinyl compound is from 0 to 10 % by mole (based on the whole copolymer) and the content of hexane is from 0 to 30 % by mole (based on the whole copolymer).

15 8. The laminate according to any one of claims 1 to 7, wherein said ethylene-vinyl acetate copolymer has a vinyl acetate content X (% by mole) and a saponification degree Y (%) of a methyl ester satisfy the following relationship:

$$X \times Y/100 \geq 10.0.$$

20 9. The laminate according to any one of claims 1 to 8, wherein said ethylene-vinyl acetate copolymer has a melt flow rate ( $200^\circ\text{C}$ , 5 kg-load) of 0.5 to 100 g/10 minutes.

10. A tubular member comprising a laminate according to any one of claims 1 to 9.

25 11. The tubular member according to claim 10, which is a tube for fuels.

12. A container comprising a laminate according to any one of claims 1 to 9.

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## ABSTRACT

A layer of a tetrafluoroethylene copolymer comprising 30 to 81 % by mole of tetrafluoroethylene and 70 to 19 % by mole of at least one other monomer and having a carbonate group in a polymer chain or at a polymer chain terminal, which has a melt flow rate of 0.1 to 100 g/10 minutes (230°C, 5 kg-load) and a melting point of 90 to 230°C and a layer of a polyolefin resin are adhered with a layer of an ethylene-vinyl acetate copolymer, which satisfies the following relationship:  $X \times Y/100 \geq 7.0$  wherein X is a vinyl acetate content (% by mole) and Y is a saponification degree of a methyl ester (%). The resulting laminate has high resistance to fuels, and the layer of the tetrafluoroethylene copolymer having a carbonate group and the layer of the polyolefin resin are firmly adhered.

# BIRCH, STEWART, KOLASCH & BIRCH, LLP

P.O. Box 747 • Falls Church, Virginia 22040-0747  
Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

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Insert Title:

LAMINATE COMPRISING FLUORINE-CONTAINING POLYMER

Fill in Appropriate  
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Prior Foreign Application(s)			Priority Claimed	
<u>238227/1999</u>	<u>Japan</u>	<u>Aug. 25, 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Month/Day/Year Filed)	Yes	No
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Raymond C. Stewart	(Reg. No. 21,066)	Terrell C. Birch	(Reg. No. 19,382)
Joseph A. Kolasch	(Reg. No. 22,463)	James M. Slattery	(Reg. No. 28,380)
Bernard L. Sweeney	(Reg. No. 24,448)	Michael K. Mutter	(Reg. No. 29,680)
Charles Gorenstein	(Reg. No. 29,271)	Gerald M. Murphy, Jr.	(Reg. No. 28,977)
Leonard R. Svensson	(Reg. No. 30,330)	Terry L. Clark	(Reg. No. 32,644)
Andrew D. Meikle	(Reg. No. 32,868)	Marc S. Weiner	(Reg. No. 32,181)
Joe McKinney Muncy	(Reg. No. 32,334)	Donald J. Daley	(Reg. No. 34,313)
John W. Bailey	(Reg. No. 32,881)	John A. Castellano	(Reg. No. 35,094)
Gary D. Yacura	(Reg. No. 35,416)		

Send Correspondence to:

**BIRCH, STEWART, KOLASCH & BIRCH, LLP**

or Customer No. 2292

P.O. Box 747 • Falls Church, Virginia 22040-0747

Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

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Full Name of First  
or Sole Inventor:  
Insert Name of  
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Full Name of Second  
Inventor, if any:  
see above

Full Name of Third  
Inventor, if any:  
see above

Full Name of Fourth  
Inventor, if any:  
see above

Full Name of Fifth  
Inventor, if any:  
see above

GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Tatsuya HIGUCHI	Tatsuya Higuchi	Feb. 19, 2002
Residence (City, State & Country)	CITIZENSHIP	
Settsu-shi, (Osaka) Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)		
c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		
GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Hidenori OZAKI	Hidenori Ozaki	Feb. 19, 2002
Residence (City, State & Country)	CITIZENSHIP	
Settsu-shi, (Osaka) Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)		
c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		
GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Takahiro KITAHARA	Takahiro Kitahara	Feb. 19, 2002
Residence (City, State & Country)	CITIZENSHIP	
Settsu-shi, (Osaka) Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)		
c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		
GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Kazuo ISHIWARI	Kazuo Ishiwari	Feb. 19, 2002
Residence (City, State & Country)	CITIZENSHIP	
Settsu-shi, (Osaka) Japan	Japan	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)		
c/o Yodogawa Works of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka 566-8585 Japan		
GIVEN NAME/FAMILY NAME	INVENTOR'S SIGNATURE	DATE*
Residence (City, State & Country)	CITIZENSHIP	
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